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Rate Constant Computation on Some Chlorination Reactions of Hg in Combustion Flue Gas

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Abstract

The geometry optimizations of reactants, products and transition states were made by the quantum chemistry MP2 method at the SDD basis function level for Hg, and 6-311++G(3df, 3pd) for others. The properties of stable minimums were validated by vibration frequencies analysis. Furthermore, the microcosmic chemical reaction mechanisms of reactions were investigated by ab initio calculations of quantum chemistry. Among these chlorination reactions involving mercury, the processes of reaction $Hg+Cl_2 \rightarrow HgCl+Cl$ and reaction $Hg+HOCl \rightarrow HgCl+OH$ are $Hg+Cl_2 \rightarrow M(HgClCl) \rightarrow TS(HgClCl) \rightarrow HgCl+Cl$ and $Hg+HOCl \rightarrow M(HgClOH) \rightarrow TS(HgClOH) \rightarrow HgCl+OH$, which include intermediates (M) that others do not have. On the basis of the geometry optimization, reaction rate constants within 200-2000K are calculated neither from experimental data nor by estimated, but directly from Quantum Chemistry software–Khimera.

Keywords：Reaction rante constant；Trace element；Quantum chemistry；Khimera

1. Introduction

With the degree of attention on Pollutants emission control gradually strengthened all over the world, and SO_2, NO_X pollutants control technology basically sound, pollutants of mercury and other trace elements have been got attention in recent years. Field studies show that coal-fired plants emit anywhere from 5% to 95% of the mercury contained in their coal [1, 2]. In the combustion process of coal-fired power plants, any form of mercury in the coal will be converted into gaseous elemental mercury and

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come into the flue gas [3]. As temperatures fall during the flow process, the favored equilibrium product shifts to $HgCl_2$. At low temperatures, approximately 10% of the mercury is predicted to be present as HgO [4, 5].

Existing forms of mercury in flue gas significantly affect the removal of mercury. Comparing with element mercury, $HgCl_2$ is water-soluble and it tends to interact with mineral matter and char. Thus, the factors that control the division of mercury between the elemental and oxidized states are thought to be of critical importance in understanding mercury emission behavior. The mechanisms about mercury conversion, however, are poorly understood. As the concentration of mercury is low and detection difficult (the interferences of sulfur dioxide SO_2 and molecular chlorine Cl_2 can cause elemental mercury to be measured as oxidized mercury [6-8]), experimental study under appropriate conditions are sparse, nor the kinetic data.

Mechanism about the oxidation of mercury for in-depth understanding of form transformation of mercury in coal combustion is essential. However, little computational studies have been done so far to understand mercury reactions using quantum chemistry [9-14]. Niksa et al. [15] developed and evaluated an elementary reaction mechanism for homogeneous Hg0 oxidation. Brown et al. [3] provided relatively comprehensive Hg chlorination pathways to date, with model predictions in good accord with experimental data for higher reactor temperatures but a drastic under prediction of Hg chlorination for lower temperatures.

In the absence of actual rate constants data for the gas-phase reactions of mercury, Arrhenius constants were experimentally determined or estimated from a variety of sources, which may led to the deviation that stated above and was commonly used by previous investigators. The rate constants can be calculated directly through using quantum chemistry and transition state theory (TST), which is the most accurate theoretical method at present. In any case, an accurate reaction rate constant is needed as a component in any Chemical reaction mechanism. The present work focuses on this goal.

2. 2. Research Programs and Computational Methods

2.1. Molecular Geometry Configuration, Optimization and the Establishment of Reaction Channel.

The reactions listed below may take place in the flue gases of coal combustion and were studied in this paper:

$$Hg+HCl \rightarrow HgCl+H \quad (1)$$

$$HgCl+HCl \rightarrow HgCl_2+H \quad (2)$$

$$HgCl+Cl \rightarrow HgCl_2 \quad (3)$$

$$Hg+Cl_2 \rightarrow HgCl+Cl \quad (4)$$

$$HgCl+M \rightarrow Hg+Cl+M \quad (5)$$

$$Hg+HOCl \rightarrow HgCl+OH \quad (6)$$

As mercury is the heavy metal owned 80 electrons, pseudopotential basis sets is necessary to make the calculations tractable while obtaining accurate theoretical rate constants. Using standard basis set, for the system which had much more electric charges, is not enough; it is needed to add diffuse functions to increase the extent of valence orbit distribution in space. Adding Polarization functions, at the same time, make the atoms more flexible in spatial orientation and easier to bond others' orbits. So the geometry optimizations of reactants, products and transition states were made by Gaussion03 [16] using the quantum chemistry MP2 method at the SDD basis function level for mercury, and 6-311++G (3df, 3pd)

for others. Each molecular parameter, e.g. energy and frequency, can get through the computational processing, and then set up the reaction channel.

2.2. Rate constant calculations.

On the basis of the above work, reaction rate constants of six chemical reaction equations have been calculated within the temperature range 200 to 2000K(every Integer points) at the constant pressure of 1.0 atm. They are calculated neither from experimental data nor by estimated, but directly from Quantum Chemistry software – Khimera(using transition state theory). Through the linear fit of ln$k$ on 1/T, the expression of reaction rate constant can be obtained. In addition, preexponential factor (A) and activation energy (Ea) will also be got by this way.

3. Results and Analyses

3.1. Geometry Optimization and Energy Comparison.

Generally speaking, the quantum mechanical method and basis set should be examined carefully in terms of their accuracy relative to experimental data. Because of the lack of experimental rate constant data available for mercury reactions, validation of accuracy of calculation results must be explored through the comparison of theoretical geometries, frequencies of vibration, and Energy change of reaction to experiment. Table 1 provides a list of comparison of molecular geometry optimization results, literature [17] results and experimental data, which were obtained from the NIST database. [18]It shows that the present work results are more accurate with an average relative error of 1.15% than the literature results with an average relative error of 5.11%.

Table 1.Comparison of Molecular Geometry Optimization. (length in Å/angle in deg)

Molecular	Bond length/ Bond angel	Present work	Literature	Experimental
HCl	r(HCl)	1.2718	1.3144	1.2746
HgCl	r(HgCl)	2.3835	2.4706	2.23
$HgCl_2$	r(HgCl)	2.273	2.3489	2.31
	a(ClHgCl)	180	180	180
Cl_2	r(ClCl)	1.9845	2.2455	1.9879
	r(HO)	0.9652	0.9968	0.96
HOCl	r(OCl)	1.6875	1.8559	1.689
	a(HOCl)	102.994	103.5	102.5
OH	r(OH)	0.9667	0.9973	0.9706

3.2. Explorations of Microscopic Reaction Mechanism

Table 2 presents a list of physical parameter of transition states and intermediates, which are involved in six reactions. Vibration frequency analyses were used to verify intermediates and transition states. It is clear that every transition state only has a single imaginary vibration frequency, which indicated transition

state is correct and credible. Intermediates were validated to be the stationary points of potential surface, because theirs vibration frequencies were all positive numbers.

On the basis of the above analysis, we could make an analysis description for microscopic reaction mechanism of every reaction. Fig.1 provides microscopic processes of six reactions. As they are showed, the processes of reaction 4 and reaction 6 are $Hg+Cl_2 \rightarrow M(HgClCl) \rightarrow TS(HgClCl) \rightarrow HgCl+Cl$ and $Hg+HOCl \rightarrow M(HgClOH) \rightarrow TS(HgClOH) \rightarrow HgCl+OH$, which include intermediates (M) that others do not have. Meanwhile all processes go through transition states (TS) except reaction 5. Reaction 5 is a direct reaction, which has no intermediate or transition state.

Table 2 Physical Parameter of Transition States and Intermediates. (length in Å/angle in deg/frequency in cm^{-1})

item	Stationary point	Bond length/ Bond angel		Vibration frequency
Reaction (1)	TS1	r(HgCl)	4.2519	-762.7105
		r(Cl-H)	3.3625	31.079
		a(HClHg)	79.62	99.6394
Reaction (2)	TS2	r(ClHg)	2.3966	-1551.1293
		r(HgCl)	2.4983	57.5421
		r(ClH)	2.244	279.2039
		a(ClHgCl)	179.68	281.245
		a(HClHg)	179.53	319.9086
		a(ClHgClH)	0	344.8341
Reaction (3)	TS3	r(ClHg)	4.562	-95.9291
		r(HgCl)	2.528	14.68
		a(ClHgCl)	87.61	245.0399
Reaction (4)	M4	r(HgCl)	3.067	53.604
		r(ClCl)	2.006	63.9878
		a(ClClHg)	179.93	521.5893
	TS4	r(HgCl)	3.8224	-25.1146
		r(ClCl)	1.9849	29.1366
		(ClClHg)	115.27	576.7502
Reaction (5)	/	/	/	/
Reaction (6)	M6	r(HgCl)	3.1384	55.4266
		r(ClO)	1.6985	77.9351
		a(OClHg)	178.61	79.2711
		r(OH)	0.9659	726.4363
		a(HOCl)	102.72	1236.6948
		a(HOClHg)	180	3818.927
	TS6	r(HgCl)	2.3596	-211.5708
		r(ClO)	2.7652	60.0856
		a(OClHg)	174.57	71.6539
		r(OH)	0.9833	328.7182
		a(HOCl)	69.81	509.0623
		a(HOClHg)	0	3618.2782

For reaction 4, $Hg+Cl_2 \rightarrow HgCl+Cl$, Hg reacts with Cl_2, absorbing some energy, to form the stable intermediate M4, and then convert to the transition state TS4 which exists in a short time. Finally TS4 break down into HgCl and free radical Cl. During the reaction process, the distance between Hg and Cl firstly elongated, then gradually shortened.

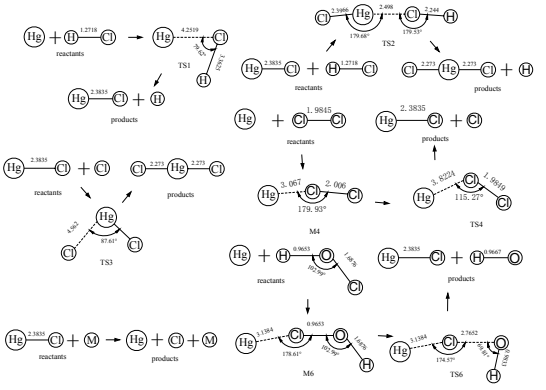

Fig.1 Microscopic Processes of Six Reactions.

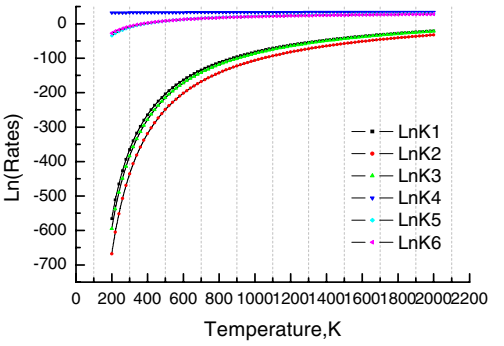

Fig.2 Change of lnk via T for Six Reactions.

For reaction 6, Hg+HOCl→HgCl+OH, Hg reacts with HOCl, absorbing some energy, to form the stable intermediate M6, and then convert to the transition state TS6 which exists in a short time. Finally TS6 breaks down into HgCl and free radical OH. During the process that M6 to products via TS6, the distance between O and Cl gradually elongated from 0.9653Å to 2.7652Å and break off at last. At the same time the bond length O-H shortened from 1.6876Å to 0.9667Å via 0.9833Å.

3.3. Rate Constant Computation.

As the geometry optimizations of molecules had been done, the reaction rate constant can be calculated. In the temperature range of 200 to 2000K (every Integer point), at the constant pressure of 1.0 atm, reaction rate constants of six reactions have been directly calculated by khimera, which is a quantum chemistry software. Fig.2 shows the change of lnk via T for six reactions. Obviously, rate constants of reactions 4 5 and 6 are larger than that of reactions 1 2 and 3. Through the linear fit of ln$k$ on 1/T, the expression of reaction rate constant are calculated, and the results are listed below.

$$k_1 = 3.472\times10^{16} e^{-19630/T} (cm^3 mol^{-1} s^{-1}) \quad (7)$$

$$k_2 = 4.619\times10^{15} e^{-14723/T} (cm^3 mol^{-1} s^{-1}) \quad (8)$$

$$k_3 = 5.641\times10^{17} e^{-30505/T} (cm^3 mol^{-1} s^{-1}) \quad (9)$$

$$k_4 = 6.055\times10^{14} e^{-139/T} (cm^3 mol^{-1} s^{-1}) \quad (10)$$

$$k_5 = 3.63\times10^{15} e^{-3357/T} (cm^3 mol^{-1} s^{-1}) \quad (11)$$

$$k_6 = 2.127\times10^{14} e^{-2952/T} (cm^3 mol^{-1} s^{-1}) \quad (12)$$

4. Conclusions

The geometries and frequencies of stationary points, containing the reactants, products, transition states and intermediates, are calculated by Gaussian 03 software, which is using the quantum chemistry theory. It is shown that the calculated results agree well with the experimental data which come from NIST database. Reaction rate constants are calculated by khimera software in the temperature range of 200-2000K with 1.0atm, meanwhile expressions of reaction rate constant obtained through the linear fit of ln$k$ on 1/T. Among these reactions, reaction 4 is the fast and reaction 2 is the slowest. In addition,

reaction 6 is faster than reaction 5 before 500K, but slower after that. Of all the reactions only reaction 5 has no intermediates or transition states, but reaction 4 is similar with reaction 6, which both has intermediate and transition state.

Due to the difficulty of measurement, there are no experimental kinetic data available to compare to the computational. Thus application of quantum chemical kinetic modeling is indispensable for this area. Reaction rate constants are critical factors for chemical kinetic model and the results we calculated can provide a reference for future research.

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